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EIGHTH ALL-UNION CONFERENCE ON THE  
CHEMISTRY OF COMPLEX COMPOUNDS

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/Following is the translation of an article (unsigned) entitled "Vosmoye Vsesoyuznoye Soveshchaniye po Khimii Kompleksnykh Soyedineniy" (English version above) in Ukrainskiy Khimicheskii Zhurnal (Ukrainian Chemistry Journal) Vol. XXV, No. 5, Kiev, 1959, pages 680-691/

## EIGHTH ALL-UNION CONFERENCE ON THE CHEMISTRY OF COMPLEX COMPOUNDS

The 8-th All-Union Conference on the Chemistry of Complex Compounds, in the work of which about 600 chemists of the Soviet Union, Czechoslovakia and Poland participated, was held at Kiev in May of this year. 97 reports were heard and discussed at the conference.

The work of the conference was carried out in three sections, which studied complex compounds in solution, the structure and stability of complex compounds, the preparation and properties of complexes of a number of metals of the platinum group, cobalt, and the rare and rare-earth elements, heteropoly acids, and the structure and configuration of crystalline complex compounds.

The conference was opened by Academician I. I. Chernyayev, President of the Orgkomitet.

Problems of the investigation of complex compounds in connection with chemical problems of the seven-year plan were considered by Academician V. I. Spitsyn, who pointed up the role of complex compounds in the production of semiconductors (ferromagnetics and ferroelectrics), in

radiochemical research, in the production of pure metals (extraction and chromatographic methods), in hydroelectrometallurgy, in the production of adhesives, in the synthesis of catalysts for the production of high polymers, and in the applications of complex ions for various purposes, including the softening of water and the dressing of ores.

Problems and results of investigation of complex formation in solutions were set forth in a number of reports.

In a report entitled "Study of Complex Formation in Solutions of Three Component Systems" A. K. Babko (Kiev) showed that in systems containing the cation of a metal, an electronegative addend, and an organic base, we may observe the formation of compounds whose properties closely resemble those of intracomplex compounds, although the "claw" bond is absent. Compounds of a new type containing one addend and two different central ions were isolated and studied. The tin-iron-dimethylglyoxime complex, which is characterized by great stability, is of this type.

The report of M. M. Tananayko (Kiev) on the results of study of ternary compounds of thiocyanates of copper, cobalt and iron with pyridine and quinoline, was devoted to the same problem.

A number of reports set forth the results of study

of complex formation between metal ions and ethylenediamine tetraacetic acid ( $H_4Y$ ): G. S. Savchenko, I. V. Tananayev, and Ye. V. Goncharov (Moscow), "Study of Complex Formation Between Aluminum, Gallium, and Indium Ions and Ethylenediamine Tetraacetic Acid in Solution by the Method of Physical-Chemical Analysis"; B. P. Nikol'skiy, A. M. Trofimov, and H. V. Vysokoostrovsk (Leningrad), "Complex Formation by Radium, Barium, and Potassium in Solutions of Ethylenediamine Tetraacetic Acid"; L. I. Martynenko and A. I. Kameneva (Moscow), "The Mechanism of Complex Formation in Ion-Exchange Separation of Rare-Earth Elements with Ethylenediamine Tetraacetic Acid". In the first of these researches, it was shown by spectrophotometric methods and by measurements of the electrical conductivity and pH of the solutions that the reaction in which the  $H_4Y$  complexes are formed with aluminum, gallium, and indium proceeds in three stages; the formation of the complex ions is reflected on the diagram in the form of sharply expressed singular points. In the second work, complex formation by barium and radium was studied on ionite KU-2 by the ion-exchange method; the anion complexes with  $H_4Y$  were identified and their instability constants determined; potassium does not form complex anions with  $H_4Y$  in noticeable quantities.

B. P. Nikol'skiy, V. V. Pal'chevskiy and R. G. Gorbunova (Leningrad) used pH measurements in their work on complex formations in inorganic redox systems to investigate complex formation in the system  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{CH}_3\text{COO}^-$  and determined the product of the graduated instability constants of the complex iron compounds which formed.

I. Koryta (Prague) reported on the rates of formation of certain cyclic compounds.

I. V. Pyatnitskiy (Kiev) indicated in a report on the stability of complexes formed by metals with oxy acids in solution that within the limits of groups of the periodic system, the stability of the complexes declines as the radii of the cation complex-forming agents increase, while within periods, stability increases with increasing charge on the cation. The stability of complexes of a metal with different oxy acids is determined by the latter's structure. In a basic medium, the complexes of trioxylglutaric acid are most stable and the complexes with tartaric, malic, and citric acids are less stable. Citric acid forms more stable complexes in acidic solutions.

A. V. Pavlinova and A. Ye. Protsenko (Chernovtsy) also held forth on the compounds of aluminum and zinc with various oxy acids. The reactions of formation of complexes of aluminum and zinc with tartaric, citric, trioxylglutaric

and saccharic acids were studied by the refractometric and potentiometric methods, as well as by measurement of electrical conductivity.

A report by Ya. D. Fridman (Frunze) was devoted to equilibrium in solutions of mixed compounds of copper, silver, mercury, lead, cadmium, antimony, bismuth and other metals. The author arrives at the conclusion that many mixed complexes possess higher stability than homogeneous compounds.

A. A. Vlehek (Prague) presented a report on an application of polarography to the study of complex compounds.

P. K. Migal' and N. Kh. Grinberg (Kishinev) reported on an investigation on the composition and stability of aquocomplexes of the metal ions.

Reports on the applications of chromatographic methods to investigation of complex compounds in solution evoked spirited discussion.

A report by D. I. Ryabchikov, A. N. Yermakov, V. K. Belyayeva, and I. N. Marov (Moscow) evaluated the possibilities of using ion exchange in study of complex compounds of multivalent ions, using as an example complex formation by zirconium and hafnium with various mono- and dibasic organic oxy acids. Ion exchange was also used by Z. A. Sheka and Ye. Ye. Kriss (Kiev) to identify complex com-

pounds in systems consisting of nitric acid and nitrates of the rare-earth elements.

R. M. Dranitskaya, A. A. Morozov, Ye. K. Tsuguy, and A. I. Gabril'chenko (Odessa) reported on the possibility of separating the green and violet modifications of chromium sulphate after their absorption by KU-1 and SBS cationites with subsequent washing with hydrochloric and sulphuric acids of different concentrations. B. N. Laskorin (Moscow) reported on new, practically important methods of separating barium and radium, zirconium and hafnium, and aluminum and gallium. It was shown that the choice of the-complex forming agents has great significance for chromatographic separation of these metal pairs.

A report on the state of molybdenum (VI) and zirconium (IV) in acid solutions as studied by the methods of electromigration and ion-exchange chromatography was submitted by B. I. Nabivanets (Kiev). The pH was established under conditions in which the polymerized anionic forms of molybdic acid, low-ionic-weight cations of molybdenum and zirconium, and anionic chloride and sulphate complexes exist.

A great deal of attention was devoted to the application of various physical methods to study of the structure of complex compounds. A report by M. Ye.



Dyatkina (Moscow) considered problems relating to the magnetic properties, absorption spectra, stability, and stereochemistry of complex compounds in the light of the crystal-field theory (ligand field). The incorrectness of conclusions based on the assumption that the crystal field is electrostatic in nature was demonstrated, and the case of the inapplicability of the crystal-field theory to account for the aromatic complexes of metals and the compounds of the transition elements with unsaturated molecules, description of which is possible within the framework of the molecular-orbit method, was pointed out.

K. B. Yatsimirskiy (Ivanovo) reported on an application of the crystal-field theory to the determination of the structure and geometrical configuration of complexes on the basis of optical and thermodynamic data. The author indicated that in the series of ions  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ , the thermodynamic characteristics (heat of formation, free energy) may be expressed for many processes (complex-, crystal-lattice-, solvate formation, etc) by a common equation of the type:

$$\varphi = \alpha N + \rho \Delta E + \text{const},$$

where  $\varphi$  is the thermodynamic characteristic,  $N$  is a value which depends on the degree of covalence of the bond ( $\alpha$  is the characteristic of the addend, and  $N$  is the atomic number of the element),  $\rho$  is

a structure characteristic dependent on the distribution of electrons in a field of definite symmetry, and  $\Delta E$  is the difference between the two basic energy levels in the ion.

A report by V. I. Belova and Ya. K. Syrkin (Moscow) entitled "Magnetic Susceptibility and Structure of Complex Compounds of Nickel, Iron, Osmium, and Ruthenium" noted the advantages and shortcomings of the ligand-field theory in accounting for the magnetic properties of the complexes. In setting forth the experimental data, note was taken of the agreement between the magnetic and x-ray structural investigations.

A report by V. N. Tolmachev, L. N. Serpukhova and T. G. Lomakina (Khar'kov) on the interrelationship between the absorption spectra of complex compounds and their stability examined the influence of the nature of the chemical bonds in the complexes on their absorption spectra and magnetic properties. The necessity of taking into account solvation processes in the solution in studying the interrelationship of the physical-chemical characteristics of complex compounds with their stability was pointed out.

G. B. Bokiy, M. N. Lyashenko, and V. I. Sokol (Moscow) submitted a report "On the Coordinate Refractions of Complex Compounds of Palladium, Rhodium, and Iridium"

A number of complex compounds of palladium, rhodium, and iridium were synthesized, their densities and the dispersion of their indices of refraction were measured, and the molecular refractions of these compounds and a series of coordinate refractions were computed. It was shown that the coordinate refraction depends chiefly on the nature of the addends and to a much lesser degree on the central atom.

In a report entitled "The Structure of Complex Compounds of Co, Ni, Cu, and Pt of the Type  $MeA_2X_2$ " by N. A. Poray-Koshits, G. N. Tishchenko and L. O. Atovmian (Moscow), it was noted that crystallographic properties common to elements of the first transition period are octahedral coordination of  $Me^{II}$ , chain combination of the  $Me^{II}$  atoms with one another through acid radicals, and two possible packing planes for the chains, the choice between which is determined by the geometry of the addends A and X. The uniqueness of the transition metals is expressed in the variation of the individual metal-addend distances, and, as a result, in various distortions of the basic packing motif. The report presented a detailed analysis of the structure of  $CoPy_2(NCS)_2$  and  $CuPy_2(NCS)_2$  crystals. The coordination isomerism characteristic of compounds of the type  $CoA_2X_2$  was studied using the ex-

ample of - and  $\beta$ -CoPy<sub>2</sub>Cl<sub>2</sub>. The structure of trans-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> was studied as an example of a compound which may have either ordered or disordered configuration.

M. I. Usanovich (Alma-Ata) showed in his report entitled "Complex Formation in the System H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub>-CH<sub>3</sub>COOH-H<sub>2</sub>O" that complex acid-base interrelationships which are further complicated by autocomplex formation in the H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> are reflected in the properties of the ternary systems which he studied. The decline in the conductivity of the acids and their mixtures when water was added to them was accounted for by the high mobility of the autocomplex ions in sulphuric and nitric acids.

D. S. Bystrov, V. N. Filimonov and A. N. Terenin (Leningrad) set forth the results of an investigation of the infrared absorption spectra of molecular compounds of a number of unsaturated hydrocarbons and organic molecules containing atoms of O, N, and S with AlCl<sub>3</sub>, AlBr<sub>3</sub>, SnCl<sub>4</sub>, TiCl<sub>4</sub>, and certain other metal halides, which are typical aprotic acids. The data obtained made it possible to resolve the question as to the structure of certain molecular compounds and the point of attachment of the halides to the organic molecules.

A number of reports were devoted to study of the complex-formation processes in nonaqueous solutions and

in aqueous-organic media. These included the work of Ya. A. Fialkov (deceased) and Z. A. Fokina (Kiev) entitled "Complex Formation Between Gallium Trichloride and Chlorides of Certain Other Elements in Nonaqueous Systems", in which various methods were used to study complex formations in the systems  $\text{GaCl}_3\text{---C}_6\text{H}_5\text{NO}_2$ ,  $\text{GaCl}_3\text{---KCl---C}_6\text{H}_5\text{NO}_2$ ,  $\text{GaCl}_3\text{---ICl---C}_6\text{H}_5\text{NO}_2$ ,  $\text{GaCl}_3\text{---PCl}_5$ ,  $\text{GaCl}_3\text{---PCl}_5\text{---C}_6\text{H}_5\text{NO}_2$ .

T. N. Sumarokova, E. Sh. Yarmukhamedova, and I. G. Litvysk (Alma-Ata) reported on the interaction between the halides of tin (IV) with amines and aminoacids in various solvents ( $\text{CHCl}_2\cdot\text{COOH}$ ,  $\text{CH}_2\text{ClCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{NO}_2$ ). New complex compounds of  $\text{SnCl}_4$  with the aminoacids and amines were separated.

In his report "On the Thermochemistry of Aquo- and Solvo Complexes", V. P. Vasil'yev (Ivanovo) made reference to the great influence of the solvent on the variation of the thermodynamic function during complex formation in solution. Data on the heats of dilution and mixture in alcohol and alcohol-water solutions enabled him to calculate the heats involved in the change in the composition of the solvate shells of the ions on transition from a mixed or nonaqueous solvent to water. New data concerning the participation of water in the equilibria of complex formation in solutions were reported by L. L. Shevchenko

(Kiev). A report by A. M. Golub, L. I. Romonenko and V. M. Samoylenko (Kiev) presented the conditions of formation of complex ions of lead with thiocyanate ions having the composition  $\text{Pb}(\text{CNS})_4^{2-}$ ,  $\text{Pb}(\text{CNS})_5^{3-}$ ,  $\text{Pb}(\text{CNS})_6^{4-}$  and  $\text{Pb}(\text{CNS})_8^{6-}$ .

A large group of reports was devoted to consideration of new data on the complex compounds of platinum and metals of the platinum group. I. I. Chernyayev, L. A. Nazarova, and V. S. Orlova (Moscow) presented information on the preparation and properties of a large number of new compounds--iodopentamines of tetravalent platinum and their derivatives--in their article "On the Pentamines of Platinum". The use of the high transactivity of iodine also made it possible to obtain such derivatives as the iodopentamine-platenitrate, -platecarbonate, and -plate-sulfate and nitropentamine. In the reports of A. A. Grinberg and A. I. Dobroboreskaya (Leningrad) "On the Problem of Detection of Cis-Platodiamines in Trans-isomers and Trans-platodiamines in Cis-isomers" and A. A. Grinberg and A. I. Stetsenko "Acidic-basic Properties of  $\text{Pt}^{2+}$  with Hydroxylamine", the authors provide an account of experimental determination and theoretical justification of the sensitivity of the reaction with potassium iodide and phenolphthalein for the detection of the cis-diamines.

Conditions were established for the determination of a cis-isomer in the trans-isomers and a trans-isomer in the cis-isomers. Data obtained in study of the change in the acid-base properties in the series  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \rightarrow [\text{Pt}(\text{NH}_2\text{OH})_4]\text{Cl}_2$  by potentiometric titration were presented. The acid-dissociation constants of the cis- and trans-isomer of  $[\text{Pt}(\text{NH}_3)_2(\text{NH}_2\text{OH})_2]\text{Cl}_2$  were calculated. A report by A. D. Troitskaya (Kazan') set forth experimental data which confirm the explanation offered by A. A. Grinberg for the transactivity of coordinate substituents as a result of their reducing properties in the reaction between potassium platinite and tricyanogen alkyl phosphites.

Kh. I. Gil'dengershel' (Leningrad) reported on the acidic properties of aquo-ions of the composition  $[\text{PtEt}_2(\text{H}_2\text{O}_2)_2]^{2+}$  and  $[\text{Pt}(\text{Et}_2\text{H}_2\text{O}_2)_2]^{2+}$ . L. M. Volshteyn (Dnepropetrovsk) showed that in the formation of intracomplex compounds containing two rings formed from the corresponding noncyclic compounds, the process of ring closure proceeds in stages. The conversion of noncyclic compounds of the type  $[\text{Pt}(\text{NH}_2\text{CH}_2\text{COOH})_2\text{X}_2]$ , where  $\text{X} = \text{Cl}$ , or  $\text{NH}_2\text{CH}_2\text{COO}^-$  into an intercomplex salt cis  $[\text{Pt}(\text{NH}_2\text{CH}_2\text{COO})_2]$  was resolved into two stages. The intermediate reaction products  $[\text{Pt}(\text{NH}_2\text{CH}_2\text{COO})(\text{NH}_2\text{CH}_2\text{COOH})\text{X}]$ , each of which contains only one cycle, were separated in the free state.

A. V. Babayeva and O. N. Yevstaf'yeva (Moscow) reported the results of studies of the infrared spectra of ammoniacal complex compounds of di- and tetravalent platinum. The influence of the composition of the coordination sphere and the configuration of the molecule of the complex compound on the frequency of deformation vibration of the ammonium was studied. It was indicated in a report by S. V. Bukhovets (Leningrad) that on reacting with acetylene under various conditions, the salts of divalent platinum yield an amorphous, unstable substance that explodes on heating; the monosubstituted acetylene derivatives decompose without explosion and with the liberation of metallic platinum; the bisubstituted acetylenes enter the internal sphere of the complex, producing relatively stable crystalline substances.

S. S. Ratsanov and Ye. D. Ruchkin (Novosibirsk) reported a new form of geometric isomerism in platinum compounds; the authors refer to this as quadratic-coordinate isomerism. In the report of A. A. Babushkin, L. A. Gridova, and A. D. Gel'man (Moscow), the authors produced a detailed analysis of the infrared spectra of complex compounds of platinum with ethylene and propylene. It is shown that the double bond  $C = C$  is converted to a single bond in ethylene and propylene when they enter the inter-



nal sphere of the platinum atom; here, the binding strength between the platinum and the atoms of carbon is of the same order of magnitude as that of a normal covalent bond. I. I. Chernyayev and A. G. Mayorova (Moscow) presented a report entitled "Thiosulfate Complex Compounds of Rhodium" in which they set forth methods of preparing these multi-nuclear compounds and established their composition and properties. N. K. Pshenitsyna, S. I. Ginzburg and L. G. Sal'skaya (Moscow) reported the synthesis of a number of complex phosphates and sulfates of iridium with the cations  $\text{Ba}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{C}_9\text{H}_{14}\text{N}^+$ . O. Ye. Zvyagintsev and S. M. Starostin (Moscow) reported on the behavior of water in acid-complex nitroso compounds of ruthenium. The behavior of the water entering into the complex varied, depending on the solvent; in organic solvents, the water in the compound appears as an ordinary addend, and in aqueous solutions we observe rapid protonic dissociation of the water in the complex.

A number of works were devoted to study of the complex compounds of cobalt. A. V. Ablov (Kishinev) delivered a report entitled "The Transinfluence of Substituents in Complex Compounds of Trivalent Cobalt with Dimethylglyoxime" and, together with A. Ya. Sychev, "Kinetics of Hydration of Halogen-bis-Dimethylglyoxime Aquocobalt".

The rate constants of hydration of  $[\text{Co}(\text{H}_2\text{O})(\text{DH})_2\text{Hal}]$  were determined and the activation energies of the hydration reaction calculated. The hydration rate diminishes in the order chloro-, bromo-, iodo-bis-dimethylglyoxime aquocobalt. The unusual sequence of the rates of hydration in the halogen-bis-dimethylglyoxime aquocobalts apparently depends on the presence of water molecules in the internal coordination sphere. V. A. Golovnya and L. A. Kokh (Moscow) reported on the carbonate complex compounds of trivalent cobalt. It was shown that when sodium cobalt hexanitrite reacts with sodium bicarbonate, the monocarbonate  $[\text{Co}(\text{NO}_2)_4\text{CO}_3]^{3-}$ , forms in accordance with the transinfluence rule, then the bicarbonate, and, in the presence of a considerable excess of sodium bicarbonate, we have the formation of the cobaltitricarbonate. The reaction of formation of the dinitrodiaminocarbonate from Erdmann's salt, to which the transinfluence rule is applicable, was studied. A. V. Babayeva and I. B. Varanovskiy (Moscow) reported "On the Reaction of Pyridine-containing Complex Compounds of Divalent Cobalt and Nickel". New compounds containing both acidic substituents of different types as well as different types of amines in the coordination sphere were synthesized. P. V. Pogorishvili, M. G. Karkarashvili and M. G. Takitishvili (Tbilisi) also reported on complex

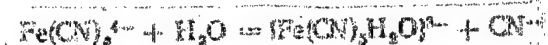
compounds of cobalt and nickel in their report entitled "Complex Compounds of Cobalt and Nickel with Ethylenediamine, Hydrazine, and Acid Hydrazides". The authors found that the transactivity of the  $\text{NO}_2$  group is higher in all cases than the transactivity of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ ,  $\text{N}_2\text{H}_4$ . A. N. Sergeyeva and K. N. Mikhailevich (L'vov) reported results of synthesis of sulphur-containing complex cobalt cyanides of the type  $\text{K}_4[\text{Co}(\text{CN})_3\text{S}_2] \cdot 6\text{H}_2\text{O}$ . The solubility, electrical conductivity and pH of aqueous solutions, and molecular weight of this compound were studied and a crystallo-optical characterization given for it. The complex acid  $\text{H}_4[\text{Co}(\text{CN})_3\text{S}_2]$  forms on reaction with mineral acids. The slightly soluble Mn, Fe, Co, Ni, Cu, and Zn salts formed by this acid, and its salts with other metals, were isolated. I. B. Khakham and I. M. Reybel' (Kishinev) reported on an investigation of the conditions of formation of binuclear cobalt ammoniates of the series decamin- $\mu$ -peroxo-dicobalt in solution. N. I. Lobanov and O. S. Konovalenko (Kishinev) presented a large volume of experimental data on the synthesis of bromates, periodates and polybromides of the cobaltamines.

Several reports were concerned with study of complex compounds of copper, zinc, and other nonferrous metals. Yan. Gazho (Bratislava) reported on the synthesis

and properties of alpha- and beta- $\text{Cu}(\text{NH}_3)_2\text{X}_2$  (where  $\text{X} = \text{Cl}$  or  $\text{Br}$ ); these studies were carried out with the purpose of investigating the reciprocal influence of addends in complex compounds of divalent copper as a function of the method by which they are prepared. The compounds were prepared from nonaqueous (acetone) media and by the dry method. The substances were recrystallized from a concentrated aqueous solution of  $\text{NH}_4\text{Br}$ . It was shown that the structure of the resulting compound depends on the methods by which they are prepared. The speaker had obtained alpha- and beta-  $\text{Cu}(\text{NH}_3)_2\text{X}_2$  whose properties were unrelated to the existence of cis- and trans-isomers. V. V. Udovenko and M. V. Artemenko (Kiev) reported on the interaction of cupric chloride and copper hydroxide with monoethanolamine; the dependence of the composition of the complex on the proportion of the components and the nature of the solvent was established.

G. A. Popovich and A. V. Ablev (Kishinev) presented extensive material on the synthesis of binary and ternary tartrates of copper (with tartrates of the alkali metals) having isomorphic structure and a complex anion of the hypothetical composition  $[\text{Cu}_2(\text{C}_4\text{H}_4\text{O}_6)_3]^{2-}$ . I. L. Kukhtevich (Dnepropetrovsk) reported on the chemical stability of  $\alpha$ - and  $\beta$ -pheophytinates of copper and zinc.

A number of reports contained experimental and theoretical material relating to the complex compounds of individual metals and nonmetals. Thus, M. N. Orlova and K. B. Yatsimirskiy (Ivanovo) reported on the kinetics and mechanism of the reaction



in the presence of gold salts and a considerable excess of the ferricyanide; this reaction follows a first-order kinetic equation with respect to the concentration of the gold not bound into the cyanide complex. A sensitive method for determining gold was worked out on this basis. A mechanism was suggested for the reaction. E. V. Ptitsyn, L. I. Vinogradova and L. L. Getskina (Leningrad) presented a description of a silver-citrate electrode and established the limits of its applicability to the determination of the instability constants of complex citrates. In a report entitled "On the Complex Compounds of Beryllium", A. V. Novoselova, K. N. Semchenko, N. Ya. Gurova and A. I. Grigor'yev (Moscow) showed that in the formation of complex oxyacetate or oxypropionate compounds of beryllium with  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{HN}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NH}_2$ , and  $\text{C}_4\text{H}_9\text{NH}_2$ , the addition reactions predominate.

The beryllium oxyacetate molecule possesses four gaps, owing to which there are vacancies in the crystal lat

tice of the salt; the presence of these accounts for the capacity of the oxyacetate or oxypropionate of beryllium to form inclusion compounds. L. P. Adamovich, I. I. Timofeyeva, B. V. Yutsis (Khar'kov) investigated aurintricarboxylic acid and the products of its reaction with beryllium. The authors established the composition of the reaction products (1 : 1), determined the instability constant, which indicated high stability over a wide concentration range, and found that the system studied is of analytical interest for visual determinations. S. N. Avakyan (Yerevan) reported on methods of preparation of mixed diamine complex compounds of the chloride and bromide of cadmium and discussed the properties of the pyridine-aniline and pyridine-ammonia complexes.

The report by M. S. Novakovskiy and M. G. Mushkina (Khar'kov) was devoted to an investigation of the formation of pyrophosphate complexes of cadmium at different pH. The composition and instability constants were determined by the emf method. G. Banag, E. Gudrinietse, and A. Ievin'sh (Riga) reported on complex compounds of arylazo- $\beta$ -diketones. Arylazo- $\beta$ -diketones obtained from the o-oxyaromatic amines, form complexes of the 1 : 1 composition with divalent metals (Cu, Cd, Co, Ni). Arylazo- $\beta$ -diketones which do not contain hydroxyl groups in the

aromatic nucleus form complexes of the composition 2 : 1 Me with the same metals. Complexes of the arylazo-  $\beta$ -diketones are absorbed onto fabrics and may be used as metallic azo dyes.

Two reports were devoted to the complex compounds of Boron. I. G. Ryss (Dnepropetrovsk) stated that the hydrolysis of coordinate compounds of boron trifluoride with a number of amines proceeds as a first-order reaction. The activation energy of hydrolysis of these compounds increases with the declining pH of the basic dissociation of the amine, while the activation entropy increases in proportion to the activation energy of the hydrolysis. V. I. Mikheyeva and V. Yu. Markina (Moscow) showed that on treatment with nitrogen-containing bases, tetraborane may decompose with the splitting off of  $\text{BH}_3$  groups and the formation of the more complex radicals  $\text{B}_3\text{H}_7$  and  $\text{H}_2\text{B}_4$ . On treatment with pyridine and trimethylamine, solids with the composition  $\text{B}_2\text{H}_4\text{NC}_5\text{H}_5$  and, hypothetically,  $[\text{BHN}(\text{CH}_3)_3]_n$ , are formed.

B. Yezhovskaya-Tshenebyatovskaya and Ya. Danovskaya (Vrotslav) reported on complex compounds of rhenium in its lower-valence forms. It had been shown earlier by polarographic and coulometric methods that a complex cyanide of rhenium forms in a solution of potassiumcyanide.

on its reduction with oxycyanorhenite. The monovalent state of the rhenium was determined by the potentiometric method. In the complex with alpha-pyridine, the rhenium occurs in the anion in the form of the monovalent element. B. Yevhovskaya-Tshebyatovskaya and L. Paydovskiy (Vrotslav) came forward with a report entitled "The Structure and Stability of Vanadium Complexes". The authors had investigated trinuclear complex compounds of vanadium,  $VAC_6(OH)_2 X \cdot yH_2O$ , which they had obtained for the first time (AC is a fatty-acid radical, and X is an organic or inorganic acid radical). Magnetic studies showed that the compounds have a three-nucleus system. The constants of formation of the complexes were determined.

F. Ya. Kul'ba and V. Ye. Mironov (Leningrad) studied the solubility of the thiocyanate and the halides of monovalent thallium in aqueous solutions of the corresponding salts of alkali metals. The instability constants of the complex cation were determined in the presence of various cations. The nature of the ions of the alkali and alkaline-earth metals has a marked influence on the process in which these complexes are formed.

A. M. Zharnovskiy (Odessa) reported on the thermal stability of bromothalliates of metals of the first and second groups of the periodic system. The anhydrous



tetrabromothalliates of the bivalent metals belong to the direct series as regards the influence of the external medium on the thermal stability of the complex anions. For tetrabromothalliates of the monovalent metals, we observe the inverse influence of the environmental ions. V. F. Toropova (Kazan') reported on the composition and stability of thiosemicarbazide complex compounds of mercury, silver, cadmium, and nickel, semicarbazide complexes of cadmium and nickel. Their instability constants were determined and used as a basis for conclusions pertaining to the nature of the bonds and the structure of the investigated compounds.

V. G. Tronev, G. K. Babeshkina, A. S. Kotel'nikova, and Myao Tsin Shen' (Moscow) reported certain new data on the "labile" and "inert" complex compounds of di-, tri-, and tetravalent rhenium. V. A. Navarenko (Odessa) reported on complex compounds of germanium with orthodiphenols and orthohydroxyquinones.

Several reports were devoted to studies of the complex compounds of the rare-earth elements and their use for separation purposes. The Plenary session heard a comprehensive report by the now deceased Ya. A. Fialkov entitled "The Rare-Earth Elements as Complex-Forming Agents", which was read by Yu. Ya. Fialkov. A report by

Ya. A. Fialkov and V. I. Vermolenko (Kiev) set forth the results of study of the formation of compounds of the rare-earth elements with salicylic acid as a function of pH and the concentration of the salicylate ion. N. V. Aksel'rud (Kiev) reported on the basic chlorides and hydroxides of the rare-earth elements, which he precipitated from aqueous solutions. Certain generalizations concerning the study of the composition and properties of these compounds were presented.

A report by S. I. Yakubson and N. A. Kostromina (Kiev) presented the results of potentiometric, conductometric, and polarometric methods of investigation, and also data on the transfer of ions in the systems of the chlorides of lanthanum, cerium, neodymium, samarium, yttrium, gadolinium, and ytterbium with gluconic acid. V. A. Golovnya and L. A. Pospelova (Moscow) synthesized a large number of sulfate and carbonate complexes of tri- and tetravalent cerium and showed that the sulfate and carbonate ions are capable of occupying one coordinate position in the internal sphere as well as two. L. A. Alekseyenko and V. V. Serebrennikov (Tomsk) cast light on the relation of complex formation in rare-earth elements with the solubility of their compounds and on complex formation in aqueous lanthanide iodide-iodine

systems. In study of the latter system, they detected the formation of polyiodides and established that the stability of the polyiodides diminishes with increasing atomic number (decreasing radii) of the extraspherical lanthanide cations. N. Ye. Brezhneva, V. I. Levin and M. G. Panova (Moscow) reported on investigation of complex formation by yttrium with o-hydroxyquinoline by the extraction method. L. S. Serbyuk and G. P. Fedorova (Dnepropetrovsk) studied the reaction of formation of a complex by a stilbase reagent with yttrium for colorimetric determination of the latter.

Investigations of complex compounds of rare elements and certain actinides belong to the same group of researches. O. A. Osipov and Yu. B. Klepenik (Rostov-on-Don) studied the electrical and thermal properties of, and carried out cryoscopic investigations on a number of complex compounds formed by the halides of zirconium with complex esters of monobasic acids. The formation of complex compounds of the types  $ZrHal_4 \cdot RCOOR_1$  and  $ZrHal_4 \cdot 2RCOOR_1$  is accompanied by a pronounced heat effect and a sharp increase in polarity (dipole moment). The complex compounds were isolated, their properties studied and their dipole moments determined. I. A. Sheka and K. F. Karlysheva (Kiev) studied the composition of cupferronates of zirconium and

hafnium obtained from hydrochloric acid, nitric acid, sulphuric acid, and hydrofluoric acid solutions. In the hydrofluoric medium, cupferronates of the composition  $\text{Me}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_4$  were formed at concentrations of the acid between 0.1 and 5 N. Cupferronates precipitated from other media are variable in composition. The solubilities of the cupferronates were determined in sulphuric, hydrochloric, nitric and hydrofluoric acid media. L. I. Budovenko (Kiev) also reported on oxalate complexes of aluminum, titanium, and zirconium. She computed the stage dissociation constants of the oxalate complexes of the zirconium and zirconyl ions. A. I. Volkova and P. Ye. Get'man (Kiev) studied salicylate complexes of titanium.

With a group of collaborators, I. I. Chernyayev investigated homogeneous complex compounds of uranyl with the carbonate, oxalate, and sulfate groups, and also mixed compounds with the same addends. They also studied thiocyanate complexes of uranyl and uranyl compounds with nitrogen-containing molecules. The compounds were isolated in the pure state and investigated in aqueous solutions by the methods of physical-chemical analysis. V. M. Vdovenko, A. A. Lipovskiy, and S. A. Nikitina (Leningrad) reported on the formation of a uranyl trichloride compound which was studied by the authors in the

process of extraction of uranium from hydrochloric acid solutions with tributyl phosphate. The spectroscopic study of uranyl nitrate solvation in organic solvents was the subject of a report by V. M. Vdovenko and D. N. Suglovoda (Leningrad). M. P. Mefed'yeva (Moscow) reported on the study of complex formation by neptunyl with acetate ions. The synthesis and study of the physical-chemical properties of certain acidocomplex compounds of uranium (IV) and cerium were the subject of a report by V. A. Golovnya and G. T. Bolotova (Moscow).

A report by I. V. Tananayeva and Lu Chzhao Da (Moscow) "On Complex Fluorides of Thorium" set forth the results of systematic study of the system  $\text{Th}(\text{NO}_3)_4$ -- $\text{NaF}$ -- $\text{H}_2\text{O}$  at low  $\text{Th}(\text{NO}_3)_4$  concentrations. The isolated solid phases were subjected to thermographic and x-ray diffraction analysis. It was shown that the interaction in this system depends on the ratio between the initial concentrations:  $\text{NaF} : \text{Th}(\text{NO}_3)_4$ . The ion  $\text{ThF}_3^+$  and some  $\text{ThF}_2^{2+}$  form with equimolar concentrations in the solution. With a large excess of sodium fluoride, it precipitates  $\text{ThF}_{3.8}\text{X}_{0.2}$  ( $\text{X} = \text{NO}_3^-$  or  $\text{OH}^-$ ); then the normal thorium fluoride forms, and with a large of excess of  $\text{NaF}$  we obtain  $\text{NaThF}_5 \cdot \text{H}_2\text{O}$ .

Problems of the investigation of heteropoly com-

pounds occupied an important position in the work of the conference and gave rise to a lively exchange of opinions. The report by V. I. Spitsyn "On the Problem of the Basicity of Heteropoly Acids and the Nature of the So-called High-Substitution Salts" presented the results of study of the reaction between small quantities of bases and the normal salts of certain heteropoly acids. It was shown that even a small increase in pH results in the formation of unsaturated heteropoly anions and the splitting-off of some of the addends of the internal sphere, instead of formation of high substitution salts, as has been affirmed in a number of published works by different authors. A. A. Babushkin, G. V. Yuhnevich, I. L. Kolli, and V. I. Spitsyn (Moscow) reported on spectroscopic investigation of the influence of water on the structure of potassium silicotungstate and the nature of its bond to the anion. They studied the infrared absorption spectra of various hydrates of potassium is-silicotungstate, as well as the spectrum of a completely dehydrated specimen. The authors suggest that water is present in two forms in potassium silicotungstate: in a constitutional form, as the hydroxyl  $W-OH$  . . . . , and a crystallization form, surrounding the anion and the hydrogen bonds related to it. V. I. Spitsyn, Ye. A. Torchenkova, and G. G. Step-

anova reported on investigation of certain rare-earth salts of cerimolybdic acid. The report by A. K. Babko and Yu. F. Shkaravskiy (Kiev) was devoted to study of extraction of heteropoly acids. According to solubility data for phosphomolybdic and silicomolybdic acids in water and in iso-butanol, and according to the distribution between the solvents under different conditions, the authors draw the conclusion that these compounds undergo polymerization in concentrated aqueous solutions. They present the optimal conditions for the separation of silicomolybdic and phosphomolybdic acids by extraction from mixed solutions.

Ye. Ya. Rode and M. M. Ivanova (Moscow) reported on a physical chemical study of heteropoly compounds of germanium. The authors synthesized germaniotungstic and germaniomolybdic heteropoly acids and the alkali metal salts of these acids, applying the methods of physical chemical analysis. The heteropoly acids studied were tetrabasic in the crystalline state; this is in agreement with the x-ray theory of the structure of these compounds. In a report by Ye. A. Nikitina and I. A. Tsvetkov (Moscow) entitled "Investigations in the Field of Isomeric  $\alpha$ - and  $\beta$ -luteophosphotungstates" reported on a new rapid method of synthesis of the  $\alpha$ - and  $\beta$ -luteophosphotungstates

of ammonium, on the preparation of the free  $\beta$ -luteophosphotungstic acid and its sodium salts in various degrees of substitution, and on the properties of the resulting compounds.

At the final session, Academician A. A. Grinberg reported on the conference on coordination chemistry held in London in April of 1959, at which Academicians A. A. Grinberg and V. I. Spitsyn of the Soviet Union participated.

It was noted in the resolution of the conference that "During recent years the significance of complex compounds has increased markedly as a result of their expanding field of application in the production of nuclear fuels and auxiliary materials for the atomic-energy industry, in the preparation of substances of high purity which are necessary for semiconductor technology, in the preparation of ferromagnetics and piezoelectrics, as catalysts for the synthesis of high polymers, for exploitation of ores of nonferreous, rare, and noble metals and the extraction of some of them in hydrometallurgical processes, to effect processes of extraction and ion exchange which are coming into wide use in various fields of technology, in construction engineering, in other branches of modern technology, biology, medicine, etc."

The conference also took note of the increasing



amount of work being done in the USSR on the theory of the chemical structure, mechanisms of reaction, and ways to the application of complex compounds, as demonstrated in the reports and numerous lectures delivered at the conference, the increased number of staff workers studying the chemistry of complex compounds, and the expansion of the fields of study.

In addition, the conference takes the position that the development of research on the theory of the chemical bond in complex compounds is lagging behind the requirements of practice. The synthesis of new types of complex compounds is proceeding at an inadequate rate.

Modern physical research methods are neglected. Few monographs and surveys dealing with the chemistry of complex compounds are being published.

The conference proposed that the chief direction of work on the chemistry of complex compounds during the next few years should be as follows:

a) Research on the synthesis of new types of complex compounds and thorough studies of their properties; this applies particularly to compounds which may prove useful in the preparation of high polymers and semiconductor materials and as catalysts for technically important processes, and other substances necessary for

technical, defense, medical, and other purposes;

b) Research on the properties of complex compounds which are already known, for the purpose of finding among them substances with semiconductor properties, piezo-electrics, and other valuable products which may be of use to modern technology;

c) The development of advanced research on the theory of the structure and reaction mechanisms of complex compounds and the application of new physical methods such as paramagnetic resonance, neutronography, radiation effects, etc., in addition to the methods presently in use for this purpose;

d) Research directed toward thorough study of the properties of complex compounds in solution, with the purpose of developing a theory and obtaining data necessary for their practical application in hydrometallurgy, chemical technology, and analytical chemistry;

e) Research on the applications of wave mechanics to the theory of the chemical bond in complex compounds and on the possibility of synthesizing new types of compounds;

f) Work on the crystal chemistry of complex compounds and the application of modern computer techniques to this work.

For successful fulfillment of the problems placed before the complex-compound chemists, the conference made the following resolutions:

1. To request the Division of Chemical Sciences of the Academy of Sciences of the USSR to include the problem "The Preparation of Complex Compounds; Study of Their Structure, Properties, and Applications" among the principal problems of chemistry and to organize a council on the problem to plan and coordinate work in this field.

2. To organize the next (ninth) conference on the chemistry of complex compounds in 1962. The place and date of the conference would be determined by the Orgkomitet.

3. To recommend small conferences on special problems of the chemistry of complex compounds, to be held between now and 1962.

4. To encourage the publication of monographs, handbooks, and surveys on individual problems of the chemistry of complex compounds, including translations and photocopied material.

5. The constant participation of representatives of Soviet science in the organization and work of international conferences on the chemistry of complex compounds is to be regarded as necessary.

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FOR REASONS OF SPEED AND ECONOMY  
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